

Predicting the Vibrational Spectra of Some Simple Fluorocarbons by Direct Scaling of Primitive Valence Force Constants

JON BAKER, PETER PULAY

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received 22 July 1997; accepted 17 November 1997

ABSTRACT: Using the scaled quantum-mechanical (SQM) force field approach with direct scaling of *individual* primitive force constants, we derive optimal scaling factors by a least-squares fit to the experimentally observed fundamentals of some selected "simple" fluorocarbons. We use the derived scaling factors to predict the vibrational spectra of all possible fluoromethanes, fluoroethylenes, fluoroethanes, and monofluoropropenes, proposing a reassignment of some experimental fundamentals. Two separate sets of scaling factors are derived for both traditional Hartree–Fock (HF) calculations and density functional theory (DFT) calculations using the hybrid three-parameter B3-PW91 density functional. With the split-valence 6-31G(d) basis set, our scaling procedure gives an average error of less than 9 cm^{-1} in the scaled frequencies with the B3-PW91 functional. The average percentage error is around 1%. The HF results are not as good—the average error is 12.6 cm^{-1} —showing that hybrid density functional SQM schemes are better for predicting vibrational spectra than basic Hartree–Fock. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 1187–1204, 1998

Keywords: vibrational spectra; SQM force fields; fluorocarbons; density functional theory

Dedicated to N. L. Allinger

Correspondence to: J. Baker

Contract/grant sponsor: U.S. Air Force Office for Scientific Research; contract/grant number: F4960-94-1-0072

Introduction

Small fluorocarbons are widely used as, among other things, lubricants, blowing and sterilizing agents, and refrigerants. Because of their increasing use, they are being extensively investigated as potential atmospheric pollutants. Their vibrational spectra are of interest both for their detection and for predicting their thermodynamic behavior. Despite much careful work over many years, the experimental identification of vibrational fundamentals is often uncertain. Theory can provide significant aid in eliminating these uncertainties.

The scaled quantum-mechanical (SQM) force field procedure¹ for predicting vibrational spectra—usually from *ab initio* (or semiempirical) force constants—is used extensively. The standard method involves first deriving a set of natural internal coordinates^{2,3} for each molecule under consideration and, on the basis of chemical intuition, sorting these into groups sharing a common scaling factor. Scaling factors for each group are determined by a least-squares fitting procedure to experimental vibrational frequencies. Force constants, originally calculated in Cartesian coordinates, are transformed into an internal coordinate representation, and scaling is applied to the elements of the internal coordinate force constant matrix (*not* to the individual vibrational frequencies) according to:

$$\mathbf{F}_{ij}(\text{scaled}) = (s_i s_j)^{1/2} \mathbf{F}_{ij} \quad (1)$$

where s_i and s_j are scaling factors for natural internal coordinates i and j , respectively. The Wilson GF matrix method⁴ is used to obtain the vibrational frequencies. The accuracy obtained by selective scaling in this way is naturally greater than if just a single overall scaling factor were used.

The SQM procedure has been widely used in the interpretation of vibrational spectra. A further important role is the development of *transferable* scale factors that can be used to modify calculated force constants and thus predict the vibrational spectrum *a priori*. For example, Rauhut and Pulay have developed a set of 11 transferable scaling factors for organic molecules containing the atoms C, O, N, and H, based on B3-LYP/6-31G* force fields,⁵ and Panchenko et al. have successfully transferred scale factors between rotational iso-

mers using HF force fields.⁶ A recent review gives several favorable comparisons between experimental IR spectra and spectra predicted using the SQM method.⁷

Recently, using the concept of a generalized inverse, first introduced in this context in the redundant optimization scheme of Pulay and Fogarasi,⁸ the original SQM procedure has been modified to allow direct scaling of *individual* primitive internal coordinates (*single* stretches, bends, and torsions),⁹ as opposed to scaling the various linear combinations of bends and torsions that are present in natural internals. The ability to scale individual primitives removes the necessity of generating natural internals, which may fail for molecules with complex topologies. Tests have shown that the resulting greater flexibility in scaling generally leads (for similar numbers of scaling factors) to somewhat better results, and more transferable scaling factors, than with natural internals.⁹

Over the past 18 months we have been investigating the ability of commonly used *ab initio* methods to predict accurately the structures and properties of simple fluorocarbons, particularly with regard to the trends observed following successive replacement of hydrogen atoms by fluorine. In previous work, we have looked at geometries, relative energies (stability), rotational barriers, and dipole moments for methane, ethylene, ethane, and all their possible fluorinated derivatives¹⁰ and, for propene, all possible monofluoropropenes and selected difluoropropenes.¹¹ Our studies showed that density functional theory using hybrid HF-DFT functionals—in particular the B3-PW91 (or ACM) functional—was perhaps the best and most cost-effective approach. It is now generally recognized that these hybrid DFT schemes can provide results of a similar quality to fairly high-level post-Hartree-Fock calculations at a fraction of the computational cost.^{12,13}

In this work we look at the vibrational frequencies of all of the fluoromethanes, fluoroethylenes, fluoroethanes, and monofluoropropenes examined in the previous two studies^{10,11} using the new primitive SQM scheme.⁹ There have been experimental determinations—mainly by jet-cooled FTIR spectroscopy—of the vibrational spectra of several of the fluorocarbons examined here during the last few years, including 1,1-difluoroethane¹⁴ and 1,1,1,2-tetrafluoroethane,¹⁵ and we use these, together with other experimental data, to derive a set of scaling factors for use with simple fluorocarbons. We then use these scaling factors to predict the fundamental frequencies and IR intensities of

the remaining fluorocarbons in our set,^{10,11} comparing our predicted frequencies with experimental values where available.

In addition to our own work,^{10,11} there has been a recent and fairly comprehensive HF and MP2 theoretical study of the fluoroethanes—including vibrational frequencies—by Papasavva et al.¹⁶ Papasavva's group tabulated experimental fundamentals for essentially all of the fluoroethanes (albeit using some rather old data). The available experimental data up to 1974 for the most stable isomer of each of the fluoroethanes were summarized by Chen et al.¹⁷ Additionally, we were able to find experimental frequencies for several of the fluoromethanes^{18–20} and fluoroethylene.²¹ However, the only monofluoropropene we could find data on was 3-fluoropropene, the latest study being a combined infrared/Raman and *ab initio* examination by Durig and coworkers.²² (The sparsity of reliable experimental data for the fluoropropenes was noted in ref. 11.)

Because one of the aims in this work is to predict the vibrational spectra of all of the monofluoropropenes, as well as to obtain scaling factors for use with other "simple" fluorocarbons, we clearly needed to include some "larger" fluorocarbons in our data set. Therefore, from the recent literature, we added 3,3,3-trifluoro-2-methylpropene,²³ 2-fluoropropane,²⁴ and 2,2-difluoropropane²⁵ to our training set. Furthermore, McNaughton (Monash University, Australia) kindly provided assigned fundamentals for 1,1,1,2,3,3,3-heptafluoropropane,²⁶ obtained by means of jet-cooled FTIR spectroscopy in a manner similar to the two other recently published studies from his group.^{14,15}

Computational Details

In line with the comments made in the Introduction, our main level of theory is DFT using the hybrid B3-PW91 functional. This uses Becke's original combination²⁷ of Slater's local exchange term,²⁸ together with the local correlation functional of Vosko, Wilk, and Nusair²⁹ (which, in turn, is a fit to the exact uniform gas results of Ceperley and Alder³⁰), Becke's nonlocal exchange functional,³¹ Perdew and Wang's nonlocal correlation functional,³² and the Hartree–Fock exchange. In previous work^{10–13} we have called this the ACM (adiabatic connection method) functional. The perhaps currently more popular B3-LYP functional is similar, but has Perdew and Wang's correlation

functional replaced by that of Lee, Yang, and Parr.³³ In addition to the DFT calculations, we also carried out standard Hartree–Fock calculations to see how the results compared. We used the split-valence 6-31G(d) basis set throughout³⁴ (with five pure spherical harmonics as opposed to six Cartesians in the *d* polarization functions).

From our previous studies we have available optimized geometries of almost all species at both levels of theory, HF/6-31G(d) and B3-PW91/6-31G(d), together with an essentially complete set of vibrational frequencies and second-derivative (Hessian) data at the Hartree–Fock level. Thus, the only additional computations needed in these cases were frequency calculations on the B3-PW91 structures. These were done using a fine grid (INT = FINEGRID) and analytical second-derivatives with Gaussian-94.³⁵ Note that geometries had previously been optimized using Turbomole,³⁶ which has a completely different DFT implementation¹³ to Gaussian, and uses a different numerical grid.³⁷ Nonetheless, in all but a couple of cases, the Turbomole-optimized geometries easily satisfied the standard convergence criteria in Gaussian-94, with failures due entirely to the displacement criteria (and this was probably the result of determining the displacement using an exact Hessian). In these cases, geometries were reoptimized to ensure a good-quality stationary point within the Gaussian implementation.

For those molecules for which converged structures were not available from earlier work—the "larger" fluorocarbons mentioned in the Introduction—geometries were optimized using the eigenvector-following (EF) algorithm³⁸ as implemented in the stand-alone optimization package Optimize.³⁹ Tight convergence criteria were used of 0.00005 a.u. on the maximum gradient component and an energy change from the previous cycle of less than 10^{-7} hartree. This ensured that the computed Hessian matrix and associated vibrational frequencies were reliable.

Results and Discussion

The following 12 molecules formed the training set from which our primitive fluorocarbon scaling factors were derived (references are to experimental gas-phase vibrational frequencies): fluoromethane,¹⁸ trifluoromethane,¹⁹ carbon tetrafluoride,²⁰ fluoroethylene,²¹ 1,1-difluoroethane,¹⁴ 1,1,1-trifluoroethane,⁴⁰ 1,1,1,2-tetrafluoroethane,¹⁵ perfluoroethane,⁴¹ 3,3,3-trifluoro-2-methyl-

propene,²³ 2-fluoropropane,²⁴ 2,2-difluoropropane,²⁵ and 1,1,1,2,3,3,3-heptafluoropropane.²⁶

The training set was chosen with some care. The quality and transferability of our least-squares scaling factors obviously depend to a large extent on the reliability of the experimental fundamentals. We used recent experimental data wherever possible as this is likely to be more accurate than earlier data. Additionally, we deliberately omitted any fluorocarbons with rotational isomers (e.g., *trans*- and *gauche*-1,1,2,2-tetrafluoroethane). Gas-phase IR spectra of molecules with two (or more) different conformers will show bands from *both* conformers, making the accurate assignment of fundamentals for a particular conformer difficult. Certain systems for which conflicting experimental data exist were also omitted from the training set (e.g., pentafluoroethane, where there are three sets of experimental vibrational frequencies in conflict with one another, usually in assignment but occasionally also in value) and we hope to be able to clarify the situation in such cases. Also, we need data to check the quality and transferability of the derived scaling factors. Some of the experimental data *are* old, especially for certain of the fluoroethanes, but were judged to be reliable.

Based on previous experience⁹ we classified all possible stretches, bends, and torsions for each system derived from standard bonding conventions into the following seven types, each of which is to be scaled separately:

1. C—H stretches.
2. C—F stretches.
3. C—C stretches.
4. H—C—H bends.
5. C—C—H and F—C—H bends.
6. C—C—C, C—C—F, and F—C—F bends.
7. All possible torsions.

Scaling factors were obtained from a least-squares fit to the experimental frequencies of all 12 molecules in the training set. Fits can be improved by using more scaling factors—for example, we could scale the C—C—H and F—C—H bends separately—but improvements are only marginal. The seven parameter types shown represent a good compromise between accuracy and number of scaling factors. Full details of the primitive SQM procedure are given in ref. 9.

Not every possible frequency for every molecule was used in the fit. In certain cases some fundamentals were simply not observed. For some systems, certain frequencies were not observed di-

rectly and were only estimates; in general, these were given zero weight in our fitting procedure. In a few cases, we questioned some of the experimental values or assignments. Details as to which fundamentals were omitted and why are given in Table I. In total we fitted 213 vibrational frequencies (out of a possible 222).

To get a rough idea as to the likely quality of the fit and to see if there were any “problem” frequencies for any of the molecules in the training set, we initially took the B3-PW91 force constants and applied the fixed scaling factors we derived for molecules containing C, O, N, H, and Cl in ref. 9. Fluorine was treated as a general first-row “heavy” (i.e., nonhydrogen) atom, and C—F bonds were scaled by the standard nonhydrogen scaling factor. Although the scaling factors in ref. 9 were derived for the B3-LYP functional instead of the B3-PW91 functional we are using here, we expect the two functionals to behave similarly.¹¹ As shown in Table I, only a few systems required “massaging.”

Only one system required a major reassignment. For 3,3,3-trifluoro-2-methylpropene,²³ there was an *A'* fundamental assigned (as a CH₂ wag) to a weak Raman band at 941 cm⁻¹, which had no apparent counterpart in the gas-phase infrared (IR) spectrum (and the data suggest that any IR signal would be at a lower frequency). After some consideration, we decided to give this mode a zero weight in our SQM fit. The major problem was with the *A'* fundamental assigned (as a CCC antisymmetric stretch) to a very strong band at 1339 cm⁻¹. The only predicted frequency in this region was a strongly IR-active mode at ~1348 cm⁻¹, which was already assigned to the CF₃ antisymmetric stretch at 1351 cm⁻¹. However, there was another strongly IR-active mode at ~1200 cm⁻¹, which we were unable to match with an assigned fundamental. Examination of the IR data (Table VIII of ref. 23) showed a strong unassigned band at 1194 cm⁻¹ that we reassigned to this *A'* mode.

The least-squares scaling factors derived for the 12 molecules in the training set, for both B3-PW91 and HF wave functions, are given in Table II. Also shown for comparison are the B3-LYP scaling factors derived for general organic molecules from the 30-molecule training set of ref. 9. Despite the different functional and the far more general nature of the training set, the scaling factors are quite similar. Note that the HF fluorocarbon scaling factors are, as expected, significantly smaller and deviate more from unity than the corresponding

TABLE I.
References and Notes to the 12 Fluorocarbons in the Training Set.

Molecule	Symmetry	Notes	No. of modes	Ref.
Fluoromethane	C_s	No omissions or reassignments	9 / 9	18
Trifluoromethane	C_s	No omissions or reassignments	9 / 9	19
Carbon tetrafluoride	T_d	No omissions or reassignments	9 / 9	20
Fluoroethylene	C_s	No omissions or reassignments	12 / 12	21
1,1-Difluoroethane	C_s	A' mode at 1171.1 cm^{-1} reassigned to A'' A'' mode at 1134.9 cm^{-1} reassigned to A'	18 / 18	14
1,1,1-Trifluoroethane	C_{3v}	Lowest mode taken from ref. 17	18 / 18	40
1,1,1,2-Tetrafluoroethane	C_s	Lowest A' mode at 225 cm^{-1} with band center uncertain given zero weight	17 / 18	15
Perfluoroethane	D_{3d}	Lowest frequency unobserved	17 / 18	41
3,3,3-Trifluoro-2-methylpropene ^a	C_s	A' mode at 941 cm^{-1} given zero weight A' fundamental at 1339 cm^{-1} reassigned to signal reported in spectrum at 1194 cm^{-1}	29 / 30	23
2-Fluoropropane	C_s	Two modes (1104 and 2960 cm^{-1}) from spectra of solid given zero weight	25 / 27	24
2,2-Difluoropropane	C_{2v}	Lowest mode (225 cm^{-1}) calculated from torsional potential given zero weight	26 / 27	25
1,1,1,2,3,3,3-Heptafluoropropane	C_s	Three fundamentals unobserved	24 / 27	26

^aThis molecule is discussed further in the text.

DFT scaling factors, showing that the HF force constants require more scaling.

Average and root-mean-square (rms) deviations between the scaled *ab initio* and experimental fundamentals for all molecules in the training set are shown in Table III. Also given is the maximum error for each molecule. As can be seen from Table III, the HF results are clearly worse, with rms and

average deviations between the scaled frequencies and experiment around 4 cm^{-1} higher than for the B3-PW91 functional. Most of the differences occur in the important fingerprint region. To give a better idea of the quality of the fit, Figure 1 shows a plot of the predicted B3-PW91/6-31G(d) infrared spectrum of 1,1,1,2-tetrafluoroethane in the range 800 to 1500 cm^{-1} , together with the experimental room temperature spectrum¹⁵ for comparison. We made no attempt to simulate the rotational band envelope; in spite of this, there is good agreement both in the peak positions and relative intensities, particularly for bands with a sharp Q branch.

Table IV gives the optimized geometries of the extra fluorocarbons we added to the training set—3,3,3-trifluoro-2-methylpropene, 2-fluoropropane, and 2,2-difluoropropane—together with experimental geometries obtained by microwave spectroscopy (heptafluoropropane was not included as we have no experimental data). Structures of these three molecules together with atom labeling corresponding to the parameters given in Table IV are shown in Figure 2. The B3-PW91 geometries are in excellent agreement with experiment, particularly the C—F bond lengths, showing once again^{10,11} the ability of this functional to make accurate geometrical predictions.

With the scaling factors from Table II, we are now in a position to predict the vibrational spectra

TABLE II.
Optimized Primitive Scaling Factors Derived from the Training Set of 12 Fluorocarbons Together with the Scaling Factors Used for General Organics Taken from Ref. 9 for Comparison.

Scaling factor		Value		
		General (ref. 9)	Fluorocarbons (this work)	
			B3-PW91	HF
Stretch	C—C	0.9207	0.9216	0.7821
Stretch	C—F		0.9248	0.7585
Stretch	C—H	0.9164	0.9125	0.8267
Bend	C—C—C	1.0144	1.0674	0.8822
	C—C—F			
	F—C—F			
Bend	C—C—H	0.9431	0.9437	0.7926
	F—C—H			
Bend	H—C—H	0.9016	0.9141	0.7894
Torsion	All	0.9523	0.9458	0.7785

TABLE III.
Average, Root-Mean-Square (rms), and Maximum Deviations between the 213 Calculated and Experimental Fundamentals for the 12 Fluorocarbons in the Training Set Using the Scaling Factors Shown in Table II.

Molecule	B3-PW91			HF		
	rms	Avg.	Max.	rms	Avg.	Max.
Fluoromethane	14.08	12.88	21.05	14.26	11.51	29.81
Trifluoromethane	11.17	9.12	17.13	28.88	21.49	65.39
Carbon tetrafluoride	10.68	7.53	25.89	17.39	13.51	34.42
Fluoroethylene	15.09	10.58	31.29	19.51	14.53	43.27
1,1-Difluoroethane	13.23	10.61	27.82	16.68	14.25	31.99
1,1,1-Trifluoroethane	10.59	9.29	16.67	13.42	9.85	32.77
1,1,1,2-Tetrafluoroethane	11.04	8.04	32.10	14.89	11.96	32.42
Perfluoroethane	8.76	7.39	17.35	16.52	12.82	46.12
3,3,3-Trifluoro-2-methylpropene	10.48	7.83	23.65	13.13	8.99	40.01
2-Fluoropropane	12.03	9.49	30.25	17.09	14.01	38.22
2,2-Difluoropropane	11.90	9.56	24.90	16.55	13.50	38.47
1,1,1,2,3,3,3-Heptafluoropropane	8.67	6.82	21.88	13.81	11.15	32.30
Total (12 molecules)	11.36	8.87	32.10	16.40	12.57	65.39
Prefingerprint region	7.54			8.75		
Fingerprint region (500–2500)	10.61			17.02		
Postfingerprint region	16.72			20.12		
Standard deviation		7.12			10.56	

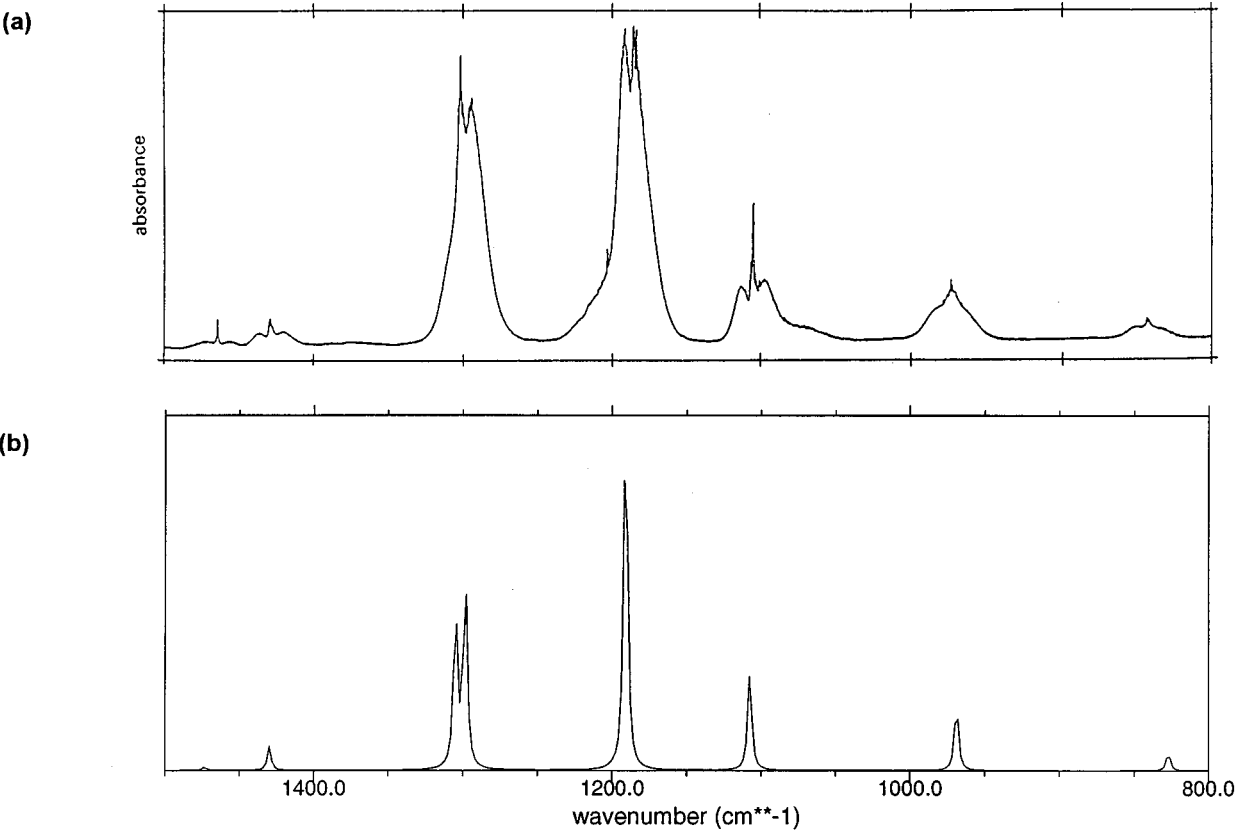


FIGURE 1. Infrared spectrum of 1,1,1,2-tetrafluoroethane from 800 to 1500 cm^{-1} : (a) room-temperature spectrum from ref. 15; (b) predicted B3-PW91/6-31G(d) spectrum using the scaling factors listed in Table II and a Lorentzian band profile with half-width 1.5 cm^{-1} .

TABLE IV.
Optimized HF and B3-PW91 Geometries (Distances in Angstroms, Angles in Degrees) for 3,3,3-Trifluoro-2-Methylpropene, 2-Fluoropropane, and 2,2-Difluoropropane with the 6-31G(d) Basis Set and Comparison with Experimental Microwave Data.

Parameter	Hartree-Fock	B3-PW91	Experiment	
3,3,3-trifluoro-2-methylpropene ^a			Ref. 24	
rC—F ₁	1.321	1.343	1.342 ± 0.005	
rC—F ₂	1.327	1.351		
rC=C	1.317	1.333	1.333 ± 0.009	
rC—C(H ₃)	1.507	1.501	1.510 ± 0.009	
rC—C(F ₃)	1.502	1.505	1.501 ± 0.009	
∠CCC(H ₃)	124.8	124.9	123.5 ± 0.8	
∠CCC(F ₃)	120.4	120.1	122.3 ± 1.9	
∠CCF ₁	113.4	113.4		
∠CCF ₂	111.1	110.9	111.6 ± 0.6	
2-Fluoropropane			Ref. 25	Ref. 43
rC—C	1.515	1.517	1.521 ± 0.007	1.515 (fixed)
rC—F	1.381	1.397	1.400 ± 0.013	1.403 ± 0.020
rC—H	1.084	1.099	1.092 (fixed)	1.095 ± 0.006
rC—H ₁	1.084	1.095	1.093 ± 0.006	1.093 (fixed)
rC—H ₂	1.085	1.096	1.094 ± 0.005	1.090 ± 0.007
rC—H ₃	1.085	1.096	1.088 ± 0.006	1.093 ± 0.005
∠CCC	114.0	113.9	113.48 ± 0.77	113.55 ± 1.17
∠FCH	106.4	106.6	106.41 (fixed)	106.62 ± 1.97
∠CCH ₁	110.3	110.4	110.04 ± 0.69	110.10 ± 2.33
∠CCH ₂	110.4	110.3	109.46 ± 0.39	109.80 ± 0.83
∠CCH ₃	110.7	110.8	110.45 ± 0.66	109.88 ± 1.00
∠CCF	108.0	108.2	108.14 ± 0.40	108.05 ± 1.83
τCCFC	123.7	123.8	123.26 ± 0.47	
2,2-Difluoropropane			Ref. 26	
rC—C	1.508	1.513	1.510 ± 0.005	
rC—F	1.354	1.375	1.378 ± 0.005	
rC—H ₁	1.083	1.094	1.091 ± 0.002	
rC—H ₂	1.083	1.094	1.091 ± 0.002	
∠CCC	116.1	116.1	116.44 ± 0.54	
∠FCF	105.9	106.2	105.15 ± 0.50	
∠CCH ₁	109.2	109.2	109.26 ± 0.05	
∠CCH ₂	110.3	110.4	109.26 ± 0.05	
τH ₁ CCH ₂	119.7		120.00 ± 0.15	

^aExperimental C—H bond lengths not reported for 3,3,3-trifluoro-2-methylpropene.

of all remaining fluoromethanes, fluoroethylenes, fluoroethanes, and monofluoropropenes. First we assess the quality of our fitted scaling factors by looking in turn at the fluoroethanes *not* included in the training set for which we have experimental data.

FLUOROETHANE (C_s)

The data here come from an early gas-phase IR and Raman study by Nielsen and coworkers.⁴³ The

experimental frequencies and their assignments, together with our predicted fundamentals, are shown in Table V. The agreement in general is very good. However, based on our results, we suggest some changes to the experimental assignments. We do not agree with the symmetry assignments of the observed bands at 1048 (A'') and 1171 (A') cm⁻¹; although the positions match nicely, both our B3-PW91 and HF results suggest that the symmetries should be switched on these two modes. Additionally, there are no frequencies

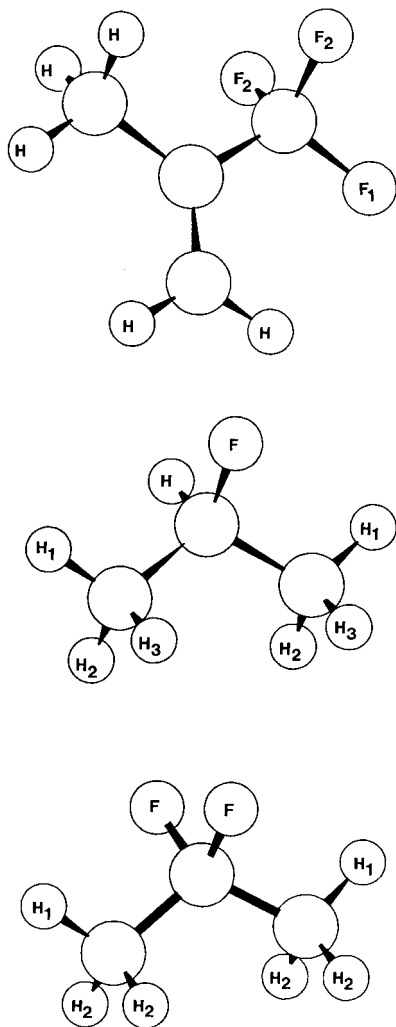


FIGURE 2. Schematic molecular structures of 3,3,3-trifluoro-2-methylpropene, 2-fluoropropane, and 2,2-difluoropropane (see Table IV).

in the theoretical spectrum that correspond to the band at 2874 cm^{-1} , which is assigned as an A'' fundamental. We consider this to be an A' combination band ($1395 + 1479 = 2874$) and instead take the band at 2967 cm^{-1} , assigned as an A' overtone ($2 \times 1479 = 2958?$), to be an A'' fundamental. If these reassignments are made, then the agreement between theory and experiment (mean deviation: 8.04 cm^{-1} B3-PW91; 13.00 cm^{-1} HF) fits nicely into the expected range. Note that the very weak signal at 278 cm^{-1} , observed only in the Raman spectrum of the liquid, was given zero weight in our least-squares fit (Chen et al.¹⁷ tabulate this frequency at 243 cm^{-1} ; however, they have several differences from the assignments of ref. 43, so we chose not to use their data).

PENTAFLUOROETHANE (C_s)

As shown in Table VI, there are at least three somewhat conflicting sets of experimental assignments for pentafluoroethane. Again, the first set comes from Nielsen's group.⁴⁴ The third set, comprising values for the low frequency fundamentals only, comes from a far infrared study by Brown et al.⁴⁶ Later, based on Raman data for C_2F_5I , Compton and Rayner proposed modified assignments for a number of C_2F_5X compounds, apparently including pentafluoroethane.⁴⁵ (It is not clear from ref. 45 where the quoted fundamentals for pentafluoroethane actually come from, as two conflicting references are given, neither of which is correct.)

There are some fundamentals below 600 cm^{-1} for which all three experimental assignments and theory agree, namely the A' fundamental at 361 cm^{-1} , the A'' at 412 cm^{-1} , and the A' at 523 cm^{-1} . Additionally, all methods agree that bands at 248 cm^{-1} and 578 cm^{-1} are fundamentals, but there is disagreement experimentally over the symmetry assignments. In general, we agree with the assignments proposed in ref. 46. The first real problem comes with the weak signal observed by Nielsen et al.⁴⁴ at 270 cm^{-1} and assigned as an A' fundamental. This assignment is not supported by our calculations or by the other two experiments and we take it to be incorrect. There is another weak signal at 508 cm^{-1} taken by both Nielsen⁴⁴ and Brown et al.⁴⁶ to be an A'' fundamental (but not by Compton and Rayner⁴⁵). The only band predicted by our SQM procedure in this region is the one at around 514 cm^{-1} (511 cm^{-1} HF), already assigned to the A' fundamental at 523 cm^{-1} . Consequently, we do not support this assignment either.

In fact theory predicts that two fundamentals, one A' and one A'' , occur very close together around 573 cm^{-1} , and it is likely that the experimental spectra hide *two* fundamentals in this region. This could explain the trouble experimentally in assigning the symmetry (two groups say A' , one A''). Nielsen's published spectrum⁴⁴ shows a strong band at 573 cm^{-1} , which has not been assigned and which *may* be the missing fundamental. In place of the band at 508 cm^{-1} , Compton and Rayner assigned a weak band at 654 cm^{-1} to an A' fundamental.⁴⁵ According to Nielsen and coworkers, this is a combination band, an assignment that is fully supported by our calculations.

For all fundamentals 725 cm^{-1} and higher, there is essential agreement between Nielsen et al.⁴⁴

TABLE V.
Predicted and Experimental (Ref. 43) Fundamentals (cm^{-1}) for Fluoroethane.^a

Experimental bands		B3-PW91			Hartree-Fock		
278 ^b vvw	A''	258	(1)	A''	240	(1)	A''
415	A'	409	(5)	A'	404	(7)	A'
810 w	A''	793	(1)	A''	779	(0)	A''
880 vs	A'	878	(10)	A'	856	(21)	A'
1048 vs	A''	1055	(59)	A'	1028	(76)	A'
1108 vs	A'	1123	(39)	A'	1102	(41)	A'
1171 s	A'	1168	(5)	A''	1158	(7)	A''
1277	A''	1275	(0)	A''	1265	(0)	A''
1365	A'	1372	(2)	A'	1376	(5)	A'
1395 vs	A'	1408	(35)	A'	1410	(35)	A'
1449 s	A' and A''	1454	(5)	A''	1443	(3)	A''
1456		1470	(2)	A'	1460	(2)	A'
1479 m	A'	1499	(1)	A'	1492	(0)	A'
2874 ms	A''	Combination band (1395 + 1479 = 2874)			Combination band (1395 + 1479 = 2874)		
2915 s	A'	2916	(51)	A'	2919	(21)	A'
2941	A'	2931	(9)	A'	2949	(37)	A'
2967 s	A' overtone (2 × 1479 = 2958)	2957	(39)	A''	2977	(2)	A''
3003 vs	A' and A''	3006	(25)	A'	2980	(51)	A'
3012 vs		3015	(34)	A''	3001	(93)	A''
rms deviation		9.83			14.90		
Average deviation		8.04			13.00		
Max. deviation		~ 20			~ 31		

^aTheoretical IR intensities in km / mole are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra.

^bVery weak, only seen in Raman spectrum of liquid (given zero weight in fit).

Compton and Raynor,⁴⁵ and our SQM results as to position, but there is some discrepancy in symmetry assignment. According to our calculations, neither group has the assignments of the frequencies at 1198, 1218, and 1309 cm^{-1} completely correct. Of the frequencies we have not reassigned, the largest difference between theory and experiment is for the A' fundamental at 1393 cm^{-1} . We have kept this value when calculating the rms and mean deviations, but we note that this *could* perhaps be a combination band (525 + 867 = 1392) and there is an IR active mode at 1447 cm^{-1} (assigned as a combination band—248 + 1198 = 1446—by Nielsen et al.⁴⁴) that gives a better fit to our predicted spectrum.

With the reassignments we have made (as shown in Table VI), the rms and average deviations (9.75 cm^{-1} B3-PW91; 13.52 cm^{-1} HF) are again in line with the other fluorocarbons we have calculated.

1,2-DIFLUOROETHANE

1,2-Difluoroethane exists in two conformers, a trans (or anti) form with the fluorine atoms diametrically opposite one another (c_{2h}) and a more stable gauche form (c_2) with an FCCF dihedral angle of around 70°. The gauche–trans energy difference is ~ 0.8 kcal/mol and the trans–gauche barrier is ~ 2 kcal/mol.¹⁰ Table VIIa shows the experimental frequencies and assignments—taken from the fairly recent IR and Raman study by Durig and coworkers⁴⁷—along with our SQM results, for both conformers. Only a few trans fundamentals have been assigned experimentally. In addition to the frequencies, Table VIIa also shows the relative IR intensities and those modes that are strongly Raman active.

Agreement between the experimental assignments and relative intensities and the SQM predictions is very good for all frequencies below 1500 cm^{-1} . However, there are some problems with the

TABLE VI.
Predicted and Experimental Fundamentals (cm⁻¹) for Pentafluoroethane.^a

Experimental bands						Theoretical fundamentals					
Ref. 44		Ref. 45		Ref. 46		B3-PW91			Hartree-Fock		
		74	A''	74	A''	63	(1)	A''	72	(1)	A''
		217	A'	217	A''	205	(2)	A''	210	(4)	A''
248	A''	247	A''	247	A'	240	(4)	A'	244	(6)	A'
270	A'										
361	A'	361	A'	361	A'	362	(0)	A'	363	(0)	A'
412	A''	413	A''	413	A''	419	(1)	A''	423	(1)	A''
508 w	A''			508	A''						
525 s	A'	523	A'	523	A'	513	(6)	A'	510	(11)	A'
573 s						572	(9)	A'	567	(12)	A'
578 s	A'	577	A''	577	A'	574	(0)	A''	572	(1)	A''
654 w	Comb.	654	A'								
725 vs	A'	725	A'			720	(28)	A'	715	(37)	A'
867 vs	A'	867	A'			858	(51)	A'	854	(73)	A'
1111 s	A'	1111	A'			1131	(110)	A'	1113	(157)	A'
1145 vs	A''	1145	A''			1149	(125)	A''	1149	(170)	A''
1198 s	A''	1198	A'			1200	(211)	A'	1207	(246)	A'
1218 vs	A'	1218	A'			1225	(326)	A''	1235	(363)	A''
1309 vs	A'	1309	A''			1309	(161)	A'	1318	(191)	A'
1359 s	A''	1359	A''			1372	(18)	A''	1370	(26)	A''
1393 m	A'	1393	A'			1433	(1)	A'	1468	(5)	A'
1447 m	Comb.										
3008 s	A'	3008	A'			2984	(31)	A'	3053	(29)	A'
rms deviation						13.70			22.31		
Average deviation						9.75			13.87		
Max. deviation						~ 40			~ 75		

^aTheoretical IR intensities (km / mole) are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra.

C—H stretches. C—H fundamentals are often difficult to assign accurately due to overlapping bands and Fermi resonances. Durig et al.⁴⁷ report six bands above 2900 cm⁻¹: a strongly Raman-active mode occurring at 2922 cm⁻¹ in the gas-phase IR spectrum, which is assigned as an overtone band; a strongly IR and Raman-active mode centered around 2958 cm⁻¹ assigned as an *A* fundamental; a mode at 2974 cm⁻¹ only(?) observed in the gas-phase Raman spectrum and assigned as an IR-inactive *A_g* mode of the trans conformer; a very intense IR band at 2985 cm⁻¹ assigned as a *B* fundamental; a strongly Raman-active mode at 2995 cm⁻¹ assigned as an *A* fundamental; and a medium intensity IR signal at 3001 cm⁻¹ assigned as a *B* fundamental. If the calculated frequencies are mapped onto these signals based solely on symmetry assignments (as has been done in Table VIIa), then the fit is fairly poor, the positions are not in good order, and there are some intensity mismatches. In particular, the very strong IR-active *B* mode at 2985 cm⁻¹ maps to a medium

intensity fundamental at 2912 cm⁻¹ (B3-PW91), an error of 73 cm⁻¹. The fit is much better if this band is mapped onto the predicted very intense IR-active fundamental at 2980 cm⁻¹.
Based on a careful comparison of observed and calculated band positions and intensities, we propose a reassignment of the C—H stretches as shown in Table VIIb. The peak at 2922 cm⁻¹, assigned experimentally as an overtone, is now considered to be a *B* fundamental. Not only the frequencies, but also the Raman intensities, now agree better (the fundamental of which this signal is a supposed overtone is calculated to be only moderately Raman active). The assignment of the 2958 cm⁻¹ band to an *A* fundamental is unchanged (and is probably contributed to by the two very close *A_g* and *B_u* modes from the trans conformer). The strongly Raman-active signal at 2974 cm⁻¹, originally assigned to a trans *A_g* mode, has been reassigned to a *B_g* mode, which is also calculated to be strongly Raman-active (and IR inactive). The other major change is with the peak

TABLE VIIa.
Predicted and Experimental (Ref. 47) Fundamentals (cm^{-1}) for 1,2-Difluoroethane.^a

Sym.	Exp.	B3-PW91	HF	Sym.	Exp.	B3-PW91	HF
A_u trans	117	133	{11}	B_u trans		1342	{17}
A	147 w	146	(3)	B	1377 m	1389	(13)
B_u trans	285 w	279	{17}	A	1410 m	1419	(19)
A	327 w	324	(0)	A_g trans		1436	—
A_g trans	457	460	—	B	1460 m	1471	(8)
B	500 m	495	(14)	A	1460 m	1474	(1)
A_u trans		799	{0}	A_g trans		1493	—
A	865 m	857	(20)	B_u trans		1502	{2}
B	896 vs	899	(39)				1496 {3}
A_g trans	1052	1059	—	Overtone	2922 ^c		
B_u trans	(1076) ^b s	1076	{186}	B_u trans		2936	{71}
A_g trans		1077	—	A	2958 ^c s	2924	(43)
B	1060 ^b s	1089	(40)	A_g trans	2974 ^c	2931	—
A	1079 vs	1098	(69)	B_g trans		2973	—
A	1116 m	1121	(16)	B	2985 vs	2912	(17)
B_g trans		1158	—	A	2995 ^c	2966	(23)
A_u trans		1208	{3}	A_u trans		2998	{76}
B	1244 m	1235	(4)	B	3001 m	2980	(58)
B_g trans		1276	—				3013 {89}
A	1284 w	1280	(1)				
			1267 (3)				

^a A and B modes derive from the C_2 gauche conformer, others (marked) from the less stable C_{2h} trans form. (Theoretical IR intensities in km / mole are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra. Allowing for the Boltzmann factor, the predicted intensities for the trans isomer { } should be scaled by ~ 0.13 at room temperature.)

^bThere appears to be a discrepancy in ref. 47 regarding the assignment of the antisymmetric (B) and symmetric (A) C—F stretches in the gauche isomer. In Table VI, these are assigned at 1060 and 1079 cm^{-1} , respectively, whereas in Table IX they are assigned at 1076 and 1079 cm^{-1} . We consider the former to be correct—the assignment to the peak at 1076 cm^{-1} is probably a typographical error. This latter peak is probably the antisymmetric C—F stretch in the trans isomer, which calculations predict to be the most intense band in the IR spectrum, and which should still give a strong signal in the experimental spectrum despite the lower concentration of the trans form.

^cStrongly Raman-active modes.

TABLE VIIb.
Alternative Assignments for C—H Stretches in 1,2-Difluoroethane.^a

Experiment	B3-PW91	Hartree-Fock
2922 ^b	Overtone	2912 (17) B
2958 ^b s	A	2924 (43) A
		2931 — A_g trans
		2936 {71} B_u trans
2974 ^b	A_g trans	2973 — B_g trans
2985 vs	B	2980 (58) B
2995 ^b	A	2966 (23) A
3001 m	B	2998 {76} A_u trans
		2948 ^b (22) B
		2962 ^b (45) A
		2968 ^b — A_g trans
		2970 {74} B_u trans
		3006 ^b — B_g trans
		3013 (69) B
		3001 ^b (28) A
		3030 {89} A_u trans

^a A and B modes derive from the C_2 gauche conformer, others (marked) from the less stable C_{2h} trans form. Relative IR intensities are given after each frequency: w—weak, m—medium, s—strong, v—very. (Theoretical IR intensities in km / mole are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra. Allowing for the Boltzmann factor, the predicted intensities for the trans isomer { } should be scaled by ~ 0.13 at room temperature.)

^bStrongly Raman-active modes.

at 3001 cm⁻¹, formerly assigned to a *B* fundamental, but now reassigned to an *A_u* fundamental of the trans conformer. This mode, which is Raman inactive, is predicted to be strongly IR active, but the lower concentration of the trans conformer results in a lower intensity signal in the observed spectrum.

With the reassignments as proposed above, the rms, average and maximum deviations between theory and experiment for all 25 assigned fundamentals are 12.94, 9.89, and ~ 34 cm⁻¹ (B3-PW91) and 16.44, 13.93, and ~ 33 cm⁻¹ (HF).

1,1,2-TRIFLUOROETHANE

The experimental data for 1,1,2-trifluoroethane come from an IR and Raman study by Kalasinsky et al.⁴⁸ There are two conformers, anti (*c₁*) and gauche (*c_s*), with the former more stable by about 1.6 kcal/mol. The gauche-anti barrier is calculated to be rather low, ~ 1 kcal/mol.¹⁰ Comparison with our calculated fundamentals is given in Table VIII. The agreement between the experimental and SQM frequencies and assignments is again good;

however, there are three problem areas in the spectrum.

The first (minor) is the band at 247 cm⁻¹, which is assigned to both an anti fundamental and an *A''* gauche fundamental. We get a nice fit for the anti conformer, but there is a better fit for the gauche with a band observed at 230 cm⁻¹; furthermore the symmetry is *A'* and not *A''*. Correspondingly, the *A'* mode at 378 cm⁻¹ should be reassigned to *A''*.

The major problem area is the 1000 to 1200 cm⁻¹ region. We have no match for the first two modes assigned by Kalasinsky et al.⁴⁸ in this region, an anti fundamental assigned to a band at 1038 cm⁻¹ only seen in the IR spectrum of the solid and an *A'* gauche fundamental assigned to the band at 1055 cm⁻¹. The closest SQM-predicted fundamentals with these symmetry assignments show good fits to other experimentally assigned fundamentals. There is another difficulty with the experimental assignment in that the band at 1100 cm⁻¹—which is the most intense in the IR spectrum—is assigned to an *A'* gauche fundamental that is calculated to be only weakly IR active (and

TABLE VIII. Predicted and Experimental (Ref. 48) Fundamentals (cm⁻¹) for 1,1,2-Trifluoroethane.^a

Sym.	Exp.		B3-PW91		HF		Sym.	Exp.		B3-PW91		HF	
A''			106	{2}	108	{3}	??	1177	vw	1161 (A')	{118}	1151 (A')	{144}
Anti	117	vw	118	(7)	113	(10)	Anti	1250	m	1241	(10)	1231	(16)
	230	vw	229 (A')	{2}	231 (A')	{3}	A''	1261 ^b		1256	{14}	1248	{21}
Anti, A''	247	w	241	(7)	243	(10)	Anti	1319	w	1327	(28)	1327	(42)
A'	378		373 (A'')	{0}	369 (A'')	{0}	A''	1361 ^b		1389	{39}	1387	{50}
Anti	426	w	429	(4)	426	(6)	Anti	1379	w	1396	(29)	1390	(36)
Anti	476	w	481	(17)	477	(25)	A'	1394		1399	{32}	1403	{34}
A'	517	vw	516	{9}	509	{13}	A'	1419		1415	{25}	1428	{37}
Anti	577	w	567	(3)	560	(5)	Anti	1433	w	1436	(16)	1450	(17)
A'	756	w	761	{46}	744	{67}	A'	1460		1473	{5}	1473	{7}
A'	869	vw	859	{34}	852	{55}	Anti	1465	w	1476	(2)	1476	(7)
Anti	905	m	896	(31)	889	(46)							
A''	941 ^b		950	{62}	948	{80}	??	2910					
Anti	1038 ^b						??	2940		2926 (A')	{9}	2966 ^c (A')	{18}
A'	1055	vw					A'	2968	w	2942	{75}	3010 ^c	{68}
Anti	1076	m	1090	(41)	1061	(119)	Anti	2974 ^c	w	2941	(21)	2977 ^c	(23)
A'	1100	s	1096	{16}	1073	{19}	Anti	2986 ^c	m	2969	(33)	3027 ^c	(10)
Anti			1108	(188)	1096	(154)	A'	2997	vw	2983 (A'')	{30}	3017 (A'')	{37}
Anti	1125	w	1123	(14)	1116	(30)	Anti	3005	s	3001	(40)	3043	(67)
A''	1148	m	1138	{90}	1132	{99}	A''	3036 ^b					
Anti	1155	m	1145	(97)	1137	(120)							

^a*A'* and *A''* modes derive from the *C_s* gauche conformer, others (marked) from the more stable *C₁* anti form. (Theoretical IR intensities in km / mole are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra. Allowing for the Boltzmann factor, the predicted intensities for the gauche isomer { } should be scaled by ~ 0.07 at room temperature.)
^bOnly seen in spectra of the solid.
^cStrongly Raman-active modes.

even weaker considering the Boltzmann factor for the less stable gauche isomer which further reduces the intensity by a factor of ~ 0.07). An alternative assignment suggested in ref. 48—that the C—F stretches for *both* conformers occur at 1100 cm^{-1} —is strongly supported by our SQM calculations. The anti fundamental at 1108 cm^{-1} B3-PW91 (1096 cm^{-1} HF) is predicted to be the most strongly IR-active mode in this molecule. There is an unassigned band at 1177 cm^{-1} in the experimental spectrum, which maps reasonably well with calculated frequencies at 1161 cm^{-1} (B3-PW91) and 1151 cm^{-1} (HF), and so we reassign this as a gauche A' fundamental.

The third and final area of discrepancy is—as was the case with 1,2-difluoroethane—the high frequency C—H stretching modes. There is a fairly good match between the experimental and SQM anti fundamentals. However, if we simply map our calculated B3-PW91 frequencies onto the assigned gauche fundamentals, the agreement is poor. The general tendency for the fluoroethanes we have examined in detail thus far is for B3-PW91 C—H stretching frequencies to be somewhat below experimental values, and the corresponding HF stretching frequencies to be somewhat above. This can be seen for pentafluoroethane (Table VI) and 1,2-difluoroethane (Table VII), and is certainly the case for the C—H stretches in the anti conformer of 1,1,2-trifluoroethane (Table VIII). Because C—H stretching frequencies are usually well isolated from other modes, their values are determined almost entirely by their corresponding bond lengths. There is a clear trend at the HF/6-31G(d) level for C—H bond lengths to *decrease* following fluorine substitution at the carbon atom concerned, mirroring the geminal effect on C—F bond lengths (e.g., see Tables 1a and 3a in ref. 10, although this trend was not commented on at the time). With DFT or MP2 this does *not* happen¹⁰; instead, C—H bond lengths tend to increase slightly following the first fluorine substitution, and thereafter remain roughly constant. (The experimental situation is unclear.) These geometrical trends result in C—H stretching frequencies for carbon atoms that are also bonded to fluorine being too high at the HF level and somewhat too low for B3-PW91, even after scaling. The best way to determine fundamentals for *individual* C—H stretching frequencies is by selective deuteration, replacing every C—H bond but one by C—D.⁴⁹

There are two unassigned bands in the experimental spectrum (shown in Table VIII) at 2910 cm^{-1} and, in particular, 2940 cm^{-1} , and if we shift

the SQM gauche fundamentals down to map with the higher of these two modes, then we conform to this general pattern and get much better agreement. This would mean assigning the unassigned band at 2940 cm^{-1} to an A' fundamental, and reassigning the A' fundamental at 2997 cm^{-1} to A'' . The band at 3036 cm^{-1} (rather high and only seen in the solid) is no longer considered as a fundamental. Although there appears to be some mismatching in signal intensities, this is readily explained by the lower Boltzmann factor of the gauche conformer.

Table VIII thus comprises our considered opinion as to the fundamental frequencies in the anti and gauche conformers of 1,1,2-trifluoroethane. With the reassignments we have proposed the rms, average, and maximum deviations between theory and experiment for 34 fundamentals (the lowest mode in the gauche conformer was not observed experimentally and we gave the A'' mode at 1361 cm^{-1} , which was only observed in the solid zero weight) are 11.46, 9.19, and $\sim 33\text{ cm}^{-1}$ (B3-PW91) and 18.01, 14.50, and $\sim 43\text{ cm}^{-1}$ (HF).

1,1,2,2-TETRAFLUOROETHANE

The experimental data here come from the same study by Kalasinsky et al., which included 1,1,2-trifluoroethane (discussed earlier).⁴⁸ There are two conformers, trans (c_{2h}) and gauche (c_2), with the former more stable by about 1.2 kcal/mol. The gauche–trans barrier is $\sim 2\text{ kcal/mol}$.¹⁰ Comparison with our calculated fundamentals is given in Table IX. As was the case with 1,1,2-trifluoroethane, the agreement between the experimental and SQM frequencies and assignments is good but there are similar problem areas.

There are two low frequency gauche modes not observed in the experimental spectrum—an A mode around 70 cm^{-1} and a B mode at $\sim 230\text{ cm}^{-1}$. Both have very low predicted IR intensities reduced even further by the lower concentration of the less stable gauche isomer, so this is perhaps not surprising. Agreement between the experimental and SQM frequencies is then excellent until the 1000 to 1200 cm^{-1} region. There are no calculated frequencies corresponding to the bands at 1075 cm^{-1} and 1081 cm^{-1} , assigned to a gauche B fundamental and a trans B_g fundamental, respectively. There is a weak IR-active gauche A fundamental calculated at $\sim 1118\text{ cm}^{-1}$ that *may* correspond to one of these bands, but the symmetry is wrong, and our best guess is that the A fundamental is hidden in the IR spectrum by the nearby

TABLE IX.
Predicted and Experimental (Ref. 48) Fundamentals (cm⁻¹) for 1,1,2,2-Tetrafluoroethane.^a

Sym.	Exp.	B3-PW91		HF		Sym.	Exp.	B3-PW91		HF	
A		67	{1}	77	{1}	B _u trans	1125 vs	1125	(210)	1103	(284)
A _u trans	82 m	78	(2)	84	(3)	B _g trans		1124	—	1125	—
A _u trans	204 m	200	(2)	204	(3)	A _u trans	1136 vvs	1145	(352)	1137	(4.17)
B		231	{5}	232	{7}	A	1146 vs	1138 (B)	{257}	1134 (B)	{292}
A	257	245	{2}	248	{3}	A _g trans	1149	1134	—	1141	—
A _g trans	362	361	—	360	—	A	1205 s	1192	{143}	1188	{169}
A	408	411	{2}	411	{3}	A	1309 s				
B _u trans	413 s	411	(43)	414	(62)	B	1312	1327	{38}	1330	{54}
B _g trans	480	491	—	491	—	B _u trans	1320 vs	1304	(39)	1307	(58)
B	523	521	{11}	516	{14}	A _u trans	1335 s	1349	(61)	1349	(82)
B _u trans	542 s	538	(7)	531	(11)	A	1362 w	1382	{28}	1381	{33}
A	598 w	591	{4}	583	{5}	B _g trans	1365	1378	—	1375	—
A _g trans	625	611	—	603	—	B	1396 w	1408	{40}	1408	{53}
B	780 m	784	{72}	775	{101}	A		1427	{3}	1458	{9}
A	906 m	898	{40}	899	{63}	A _g trans	1442	1450	—	1477	—
B	1075 w										
B _g trans	1081					B	2995 ^b	2965	{29}	3032 ^b	{28}
A _g trans	1106	1107	—	1091	—	A _g trans	2995 ^b	2975	—	3043 ^b	—
A		1118	{8}	1115	{4}	B _u trans	2995 m	2986	(68)	3052	(65)
B	1119 m	1121	{63}	1102	{101}	A	3003 m	2974	{54}	3042 ^b	{54}

^aA and B modes derive from the C₂ gauche conformer, others (marked) from the more stable C_{2h} trans form. (Theoretical IR intensities in km / mole are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra. Allowing for the Boltzmann factor, the predicted intensities for the gauche isomer { } should be scaled by ~ 0.26 at room temperature.)
^bStrongly Raman-active modes.

B fundamental at 1119 cm⁻¹. Similarly, we find a trans B_g mode at ~ 1124 cm⁻¹, which is weakly Raman active (and IR inactive) that lies almost on top of the very strongly IR-active (and Raman inactive) B_u fundamental at 1125 cm⁻¹. Thus, the strong absorption at 1125 cm⁻¹ in the IR spectrum is due to the B_u fundamental, whereas the weak signal at the same frequency in the Raman spectrum is probably due to the B_g.

The next disagreement is the strong band observed in the IR spectrum at 1146 cm⁻¹ and assigned as a gauche A fundamental. The most intense band in our predicted SQM spectrum of the gauche conformer is one at 1138 cm⁻¹ (B3-PW91), which fits nicely, but has B symmetry. Based on the predicted intensity match, we consider the experimental symmetry assignment to be incorrect. The final discrepancy is the strong band observed in the IR spectrum (but apparently Raman inactive) at 1309 cm⁻¹ assigned as a gauche A fundamental. In place of this, we predict a very weak IR-active A fundamental at ~ 1427 cm⁻¹ (B3-PW91). There is no reasonable gauche fundamental to match this band. One possibility is that this is not a new fundamental, but is in fact the same B fundamental responsible for the band in

the Raman spectrum at 1312 cm⁻¹, misassigned as having A symmetry.

In the C—H stretch region, Kalasinsky et al.⁴⁸ assigned three modes to the band centered around 2995 cm⁻¹, a gauche B fundamental and A_g and B_u trans fundamentals, with the remaining gauche A fundamental assigned to a band at 3003 cm⁻¹. Based primarily on the IR and Raman intensities, we switch the assignments of the A and B_u modes, with the B_u mode being the one at higher frequency. This would also bring the SQM fundamentals into better order.

With our reassignments, the rms, average, and maximum deviations between theory and experiment for 31 fundamentals in trans and gauche 1,1,2,2-tetrafluoroethane are 12.39, 10.07, and ~ 30 cm⁻¹ (B3-PW91) and 20.41, 14.95, and ~ 49 cm⁻¹ (HF).

PREDICTIONS FOR REMAINING FLUOROCARBONS

Our analysis of the SQM-predicted vibrational frequencies of the fluoroethanes that were not included in the training set (Tables V to IX) gives us

some confidence that we can reliably predict the fundamental vibrations of other “simple” fluorocarbons using B3-PW91/6-31G(d) force constants and the set of seven scaling factors given in Table II. We would expect an *average* error in the positions of the predicted fundamentals of around 10 cm^{-1} , a maximum error in the fingerprint region (500 to 2000 cm^{-1}) of around 20 cm^{-1} , and a maximum overall error (including the difficult C—H stretching region) of between, say, 30 and 40 cm^{-1} .

One of our main aims in this work is to predict the vibrational frequencies of the monofluoropropenes. None of the monofluoropropenes were included in the training set (although we did include 3,3,3-trifluoro-2-methylpropene) due to the lack of experimental data. However, there *are* fairly extensive experimental data for 3-fluoropropene. Apart from the latest study by Durig et al.,²² there have been general studies of the allyl halides, including 3-fluoropropene, by Gross and Forel⁵⁰ and McLachlan and Nyquist.⁵¹ A detailed comparison of the SQM-predicted vibrational frequencies

of 3-fluoropropene with experiment (based mainly on ref. 22) is given in Table X.

3-Fluoropropene has two conformers, a *cis* conformer (with all four nonhydrogen atoms in the same plane; c_s) and a *gauche* (c_1). The *cis* conformer is more stable, although there is disagreement as to the energy difference (however, it is certainly small, < 1 kcal/mol). The *cis*–*gauche* rotational barrier is ~ 3 kcal/mol.¹¹

The agreement between the calculated and experimental frequencies is generally good apart from—as was the case with some of the fluoroethanes—the C—H stretching fundamentals. Agreement with the highest frequencies is good. Agreement is not so good, although within our estimate for the expected maximum error, for the three frequencies near 3000 cm^{-1} . The worst agreement for B3-PW91 is with the two lowest C—H stretching frequencies, particularly the A' fundamental assigned to the signal at 2948 cm^{-1} . There are two (unassigned) peaks listed by Durig et al.²² at 2894 cm^{-1} and 2908 cm^{-1} , respectively, which would give a much better fit (the peak at 2894

TABLE X.
Predicted and Experimental (Ref. 22) Fundamentals (cm^{-1}) for 3-Fluoropropene.^a

Sym.	Exp.	B3-PW91	HF	Sym.	Exp.	B3-PW91	HF
Gauche	108 w	116 {1}	105 {2}	A'	1293 ^b vw	1283 (0)	1278 (1)
A''	164 m	173 (3)	159 (4)	Gauche		1284 {0}	1276 {0}
A'	268 m	266 (2)	268 (3)	Gauche	1358 s		
Gauche	332 s	324 {6}	326 {8}	Gauche	1368 s	1369 {16}	1369 {28}
Gauche	421 m	437 {3}	430 {3}	A'	1389 s	1392 (12)	1399 (18)
A''	549 s	544 (9)	544 (8)	A'	1417 s	1406 (11)	1414 (15)
A'	604 m	608 (4)	600 (9)	Gauche	1432 s	1426 {23}	1429 {29}
Gauche	641	635 {7}	625 {7}	A'	1468 m	1473 (3)	1477 (1)
A'	905	891 (1)	866 (3)	Gauche	1468	1475 {1}	1480 {1}
Gauche	920	907 {3}	893 {5}	Gauche	1646	1677 {0}	1672 {0}
A''	928 vs	921 (43)	961 (51)	A'	1653 ^b m	1680 (4)	1674 (2)
Gauche	938	933 {45}	954 {20}				
Gauche	971	970 {3}	966 {43}	??	2894 s		
A'	973 vs	993 (35)	983 (50)	??	2908		
A''	996 vs	999 (12)	991 (7)	Gauche	2938 vs	2903 {43}	2945 {50}
Gauche	996	1011 {25}	1010 {9}	A'	2948	2890 (46)	2934 (52)
A''	1032 vs	1023 (10)	1033 (18)	A''	2960 s	2923 (44)	2968 (56)
Gauche	1032	1046 {107}	1029 {152}	Gauche	2968	2955 {36}	2992 {39}
A'	1118 s	1121 (48)	1102 (54)	A'	2998 ^b s	3028 (13)	3029 (18)
Gauche	1160	1161 {1}	1146 {3}	Gauche	2998	3025 {12}	3026 {18}
Gauche	1243 s	1238 {3}	1236 {4}	Gauche	3008 ms	3040 {7}	3047 {8}
A''	1253 m	1232 (0)	1233 (0)	A'	3032 s	3047 (5)	3048 (9)
				Gauche	3100 s	3108 {14}	3102 {20}
				A'	3114	3128 (7)	3121 (11)

^a A' and A'' modes derive from the C_s *cis* conformer, others (marked) from the less stable C_1 *gauche* form. (Theoretical IR intensities in km / mole are given in parentheses; experimental bands with no quoted IR intensity are from Raman spectra. Allowing for the Boltzmann factor, the predicted intensities for the *gauche* isomer { } should be scaled by ~ 0.36 at room temperature.)

^bStrongly Raman-active modes.

TABLE XI.
Predicted Fundamentals (cm^{-1}) and IR Intensities (km / mole) for Various Fluorocarbons Using a Primitive SQM B3-PW91 / 6-31G(d) Force Field and the Seven Scaling Factors Given in Table II.

Sym.	Freq.	Intensity	Sym.	Freq.	Intensity	Sym.	Freq.	Intensity
Difluoromethane (c_{2v})			<i>Cis</i> -1,2-difluoroethylene (c_{2v})			Trifluoroethylene (c_s)		
A_1	533	1.5	A_1	229	2.1	A'	231	3.9
B_2	1107	209.7	A_2	494	—	A''	301	4.0
A_1	1112	100.1	B_1	775	34.4	A'	493	1.2
B_1	1162	19.3	B_2	780	32.7	A''	558	1.0
A_2	1245	—	A_2	837	—	A'	629	2.3
B_2	1457	46.1	A_1	1008	57.8	A''	762	30.6
A_1	1504	4.4	B_2	1137	104.0	A'	927	59.0
A_1	2934	54.1	A_1	1262	33.8	A'	1167	134.0
B_1	2997	73.0	B_2	1383	36.8	A'	1267	178.9
			A_1	1736	46.8	A'	1371	120.4
			B_2	3095	0.3	A'	1798	69.5
			A_1	3118	13.3	A'	3135	6.8
1,1-Difluoroethylene (c_{2v})			<i>Trans</i> -1,2-Difluoroethylene (c_{2h})			Perfluoroethylene (d_{2h})		
B_2	443	0.6	B_u	319	11.2	A_u	192	—
A_1	562	3.0	A_u	334	5.0	B_{2u}	207	4.5
B_1	621	1.9	A_g	556	—	A_g	403	—
A_2	704	—	B_g	791	—	B_{3u}	415	3.8
B_1	791	88.9	A_u	902	59.2	B_{2g}	498	—
A_1	923	65.5	A_g	1154	—	B_{3g}	559	—
B_2	946	15.5	B_u	1166	262.4	B_{1u}	561	0.6
B_2	1331	222.5	A_g	1278	—	A_g	779	—
A_1	1375	2.3	B_u	1279	35.2	B_{1u}	1182	360.1
A_1	1747	276.9	A_g	1721	—	B_{2u}	1329	384.2
A_1	3092	5.1	B_u	3103	15.2	B_{3g}	1358	—
B_2	3187	0	A_g	3111	—	A_g	1874	—
<i>Cis</i> -1-fluoropropene (c_s)			<i>Trans</i> -1-fluoropropene (c_s)			2-Fluoropropene (c_s)		
A''	143	0	A''	205	0.8	A''	198	0.5
A'	249	3.4	A''	280	0	A'	399	0.5
A''	421	14.2	A'	293	1.7	A''	473	1.6
A'	681	1.0	A'	534	9.7	A'	479	5.4
A''	755	28.4	A''	795	5.1	A''	736	0.1
A'	912	2.2	A'	914	8.5	A'	838	14.7
A''	912	0.1	A''	934	45.7	A''	840	69.2
A'	1010	80.5	A''	1042	0	A'	942	29.2
A''	1042	0.8	A'	1101	30.7	A'	1010	6.5
A'	1134	21.7	A'	1159	116.6	A''	1055	2.8
A'	1247	32.2	A'	1261	6.2	A'	1285	82.3
A'	1360	9.2	A'	1318	1.9	A'	1375	13.6
A'	1402	10.2	A'	1391	1.8	A'	1400	18.4
A''	1458	8.4	A''	1450	7.6	A''	1441	8.1
A'	1460	1.2	A'	1465	8.0	A'	1456	8.9
A'	1710	51.5	A'	1711	55.0	A'	1710	96.7
A'	2914	25.7	A'	2909	28.7	A'	2922	14.0
A''	2965	21.0	A''	2964	21.8	A''	2981	12.3
A'	3019	7.9	A'	2991	19.1	A'	3027	11.4
A'	3055	4.8	A'	3055	12.5	A'	3064	0
A'	3089	21.6	A'	3068	15.6	A'	3151	3.9

cm^{-1} to the A' mode calculated at 2890 cm^{-1} , and the one at 2908 cm^{-1} to the gauche mode calculated at 2903 cm^{-1}). In support of this reassignment, we note that Gross and Forel⁵⁰ assigned C—H stretching fundamentals in a number of allyl species in the range 2842 to 2920 cm^{-1} , with assignment of an A' mode for 3-fluoropropene at 2886 cm^{-1} . However, McLachlan and Nyquist later disputed this,⁵¹ suggesting that signals in the vibrational spectra of alkyl halides occurring in the range 2870 to 2905 cm^{-1} were due to the first overtone of CH_2 bending (although this is not a good explanation for 3-fluoropropene, where these bends are assigned at 1417 cm^{-1} and 1432 cm^{-1}). We are hesitant to make this reassignment because: (i) we would then have no assignment for the very strong signal in the IR spectrum at 2938 cm^{-1} ; and (ii) the HF frequencies for these two modes are actually in good agreement.

The only other discrepancy is with the strongly IR-active band at 1358 cm^{-1} assigned to a gauche fundamental. The only calculated frequency that could be matched with this is the gauche fundamental at 1284 cm^{-1} (B3-PW91); however, this is predicted to be almost IR inactive. Our judgment is that the signal at 1358 cm^{-1} is *not* a fundamental, and the gauche fundamental is instead masked (in the Raman spectrum) by the strongly Raman-active A' cis fundamental at 1293 cm^{-1} (both fundamentals are only weakly IR active).

Leaving the C—H stretch assignments unchanged, the rms and average deviations between theory and experiment for all 42 fundamentals are 18.06 and 13.50 cm^{-1} (B3-PW91) and 16.81 and 13.17 cm^{-1} (HF). The B3-PW91 deviations are somewhat worse than we would like, and worse than all the other fluorocarbons discussed so far, but we stress that the higher-than-expected error is due entirely to the C—H stretches (for which the experimental assignment may be incorrect in any case). If these are omitted then we get revised rms and average errors (for 32 fundamentals) of 11.79 and 9.30 cm^{-1} , respectively.

Table XI presents predicted fundamentals and absolute IR intensities for the remaining fluorocarbons we consider in this work for which we have no experimental data. These are: difluoromethane, 1,1-difluoroethylene, *cis*-1,2-difluoroethylene, *trans*-1,2-difluoroethylene, trifluoroethylene, perfluoroethylene, *cis*-1-fluoropropene, *trans*-1-fluoropropene, and 2-fluoropropene. We hope experimental groups will be able to confirm our predictions in the near future.

Conclusions

We have derived a set of seven primitive scaling factors for use in an SQM force field procedure for predicting the fundamental vibrational frequencies in "simple" fluorocarbons. We have presented two sets of scaling factors based on computed B3-PW91/6-31G(d) and HF/6-31G(d) force constants. The former model is the recommended one, and we expect predicted vibrational frequencies using this model to have an average error of around 10 cm^{-1} , a maximum error in the fingerprint region of around 20 cm^{-1} , and a maximum overall error of between 30 and 40 cm^{-1} (with this maximum occurring mainly for the high-frequency C—H stretches).

Using our recommended primitive SQM model we have clarified the vibrational assignments in pentafluoroethane; proposed reassignments of some of the fundamentals in fluoroethane, 1,1,2-trifluoroethane, 1,1,2,2-tetrafluoroethane, and 3,3,3-trifluoro-2-methylpropene; and proposed some tentative reassignments among the C—H stretching modes in 3-fluoropropene and 1,2-difluoroethane. Finally, we have predicted, *a priori*, the fundamental frequencies and relative IR intensities for 1,2-difluoromethane, all three difluoroethylenes, trifluoroethylene, perfluoroethylene, *cis*-1-fluoropropene, *trans*-1-fluoropropene, and 2-fluoropropene.

Acknowledgments

We are grateful to Dr. A. Jarzecki for help in locating some of the references and useful discussions, and to Dr. D. McNaughton (Monash University) for making available experimental FTIR fundamentals for 1,1,1,2,3,3,3-heptafluoropropane prior to publication.

References

1. P. Pulay, G. Fogarasi, G. Pongor, J. E. Boggs, and A. Vargha, *J. Am. Chem. Soc.*, **105**, 7037 (1983).
2. P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, **101**, 2550 (1979).
3. G. Fogarasi, X. Zhou, P. W. Taylor, and P. Pulay, *J. Am. Chem. Soc.*, **114**, 8191 (1992).
4. E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.
5. G. Rauhut and P. Pulay, *J. Phys. Chem.*, **99**, 3093 (1995).

6. Y. N. Panchenko, G. R. De Maré, and V. I. Pupyshev, *J. Phys. Chem.*, **99**, 17544 (1995).
7. P. Pulay, *J. Mol. Struct.*, **347**, 293 (1995).
8. P. Pulay and G. Fogarasi, *J. Chem. Phys.*, **96**, 2856 (1992).
9. J. Baker, A. A. Jarzecki, and P. Pulay, *J. Phys. Chem.*, in press.
10. M. Muir and J. Baker, *Mol. Phys.*, **89**, 211 (1996).
11. J. Baker and M. Muir, *J. Fluorine Chem.*, in press.
12. J. Baker, M. Muir, J. Andzelm, and A. Scheiner, In *Chemical Applications of Density Functional Theory*, B. V. Laird, T. Ziegler, and R. Ross, Eds., American Chemical Society, Washington, DC, 1996, p. 342, and references therein.
13. A. Scheiner, J. Baker, and J. Andzelm, *J. Comput. Chem.*, **18**, 775 (1997).
14. D. McNaughton and C. Evans, *J. Phys. Chem.*, **100**, 8660 (1996).
15. D. McNaughton, C. Evans, and E. G. Robertson, *J. Chem. Soc. Faraday Trans.*, **91**, 1723 (1995).
16. S. Papasavva, K. H. Illinger, and J. E. Kenny, *J. Phys. Chem.*, **100**, 10100 (1996), and references therein.
17. S. S. Chen, A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **4**, 441 (1975), and references therein.
18. J. L. Duncan, D. C. McKean, and G. K. Speirs, *Mol. Phys.*, **24**, 553 (1972).
19. I. P. Herman and J. B. Marling, *J. Phys. Chem.*, **85**, 493 (1981).
20. L. H. Jones, C. Kennedy, and S. Ekberg, *J. Chem. Phys.*, **69**, 833 (1978).
21. G. R. Smith and W. A. Guillory, *J. Chem. Phys.*, **63**, 1311 (1975).
22. (a) J. R. Durig, M.-Z. Zhen, H. L. Heusel, P. J. Joseph, P. Groner, and T. S. Little, *J. Phys. Chem.*, **89**, 2877 (1985); (b) J. R. Durig, T. J. Geyer, T. S. Little, and D. T. Durig, *J. Mol. Struct.*, **172**, 165 (1988).
23. G. A. Guirgis, J. R. Durig, and Y. S. Li, *J. Chem. Phys.*, **83**, 1507 (1985).
24. J. R. Durig, H. Nanaie, and G. A. Guirgis, *J. Raman Spectrosc.*, **22**, 155 (1991).
25. H. Nanaie, G. A. Guirgis, and J. R. Durig, *Spectrochim. Acta*, **49A**, 2039 (1993).
26. D. McNaughton, C. Evans, and E. G. Robertson, *Mikrochim. Acta (Suppl.)*, **14**, 543 (1997).
27. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
28. J. C. Slater, *Quantum Theory of Molecules and Solids*, Vol. 4, McGraw-Hill, New York, 1974.
29. S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.*, **58**, 1200 (1980).
30. D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.*, **45**, 566 (1980).
31. A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988).
32. J. P. Perdew, In *Electronic Structure of Solids*, P. Ziesche and H. Eschrig, Eds., Akademie, Berlin, 1991.
33. C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, **37**, 785 (1988).
34. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).
35. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzales, and J. A. Pople, *Gaussian-94, revision C.3*, Gaussian, Inc., Pittsburgh, PA (1995).
36. R. Ahlrichs, M. Bär, M. Ehrig, M. Häser, H. Horn, and C. Kölmel, *Turbomole*, v. 2.3, Biosym Technologies, San Diego, CA.
37. O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, **102**, 346 (1995).
38. J. Baker, *J. Comput. Chem.*, **7**, 385 (1986).
39. J. Baker, *Optimize*, a suite of algorithms for geometry optimization.
40. J. R. Nielsen, H. H. Claassen, and D. C. Smith, *J. Chem. Phys.*, **18**, 1471 (1950).
41. J. R. Nielsen, C. M. Richards, and H. L. McMurry, *J. Chem. Phys.*, **16**, 67 (1948).
42. M. Hayashi and C. Ikeda, *J. Mol. Struct.*, **223**, 207 (1990).
43. D. C. Smith, R. A. Saunders, J. R. Nielsen, and E. E. Ferguson, *J. Chem. Phys.*, **20**, 847 (1952).
44. J. R. Nielsen, H. H. Claassen, and N. B. Moran, *J. Chem. Phys.*, **23**, 329 (1955).
45. D. A. C. Compton and D. M. Rayner, *J. Phys. Chem.*, **86**, 1628 (1982).
46. F. B. Brown, A. D. H. Clague, N. D. Heitkamp, D. F. Koster, and A. Danti, *J. Mol. Spectrosc.*, **24**, 163 (1967).
47. J. R. Durig, J. Liu, T. S. Little, and V. F. Kalasinsky, *J. Phys. Chem.*, **96**, 8224 (1992).
48. V. F. Kalasinsky, H. V. Anjaria, and T. S. Little, *J. Phys. Chem.*, **86**, 1351 (1982).
49. D. C. McKean, J. E. Boggs, and L. Schäfer, *J. Mol. Struct.*, **116**, 313 (1984).
50. B. Gross and M.-T. Forel, *J. Chim. Phys.*, **62**, 1163 (1965).
51. R. D. McLachlan and R. A. Nyquist, *Spectrochim. Acta*, **24A**, 103 (1968).